4. Quantum Harmonic Oscillator

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Taylor Series

For a function $f(x)$ that is differentiable infinitely many times,

$$f(x) = a_0 + a_1(x - x_0) + a_2(x - x_0)^2 + \cdots a_n(x - x_0)^n + \cdots$$
$$= \sum_{n=0}^{\infty} a_n(x - x_0)^n.$$

The coefficients a_n are

$$a_n = \frac{f^{(n)}(x_0)}{n!} = \frac{1}{n!}\frac{d^n f(x)}{dx^n}\bigg|_{x=x_0}.$$

For example,

$$(e^{i\theta} = \cos\theta + i\sin\theta)$$

$$e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!}, \quad \sin x = \sum_{n=0}^{\infty}(-1)^n\frac{x^{2n+1}}{(2n+1)!}, \quad \cos x = \sum_{n=0}^{\infty}(-1)^n\frac{x^{2n}}{(2n)!}.$$

Series Solution of the Differential Equation

As an example, let us return to the homogenous DE

$$y''(x) + k^2 y(x) = 0 \quad \rightarrow \quad y(x) = A\cos(kx) + B\sin(kx)$$

which is readily solved based on the auxiliary equation.

Alternatively, we can assume a solution of the form

$$y(x) = \sum_{n=0}^{\infty} a_n x^n,$$

which leads to

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} + k^2 \sum_{n=0}^{\infty} a_n x^n = 0,$$

when inserted in the DE.

Series Solution of the Differential Equation

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} + k^2 \sum_{n=0}^{\infty} a_n x^n = 0$$

Grouping the terms with the same power gives the recursion relation

$$a_{n+2} = -\frac{k^2}{(n+1)(n+2)} a_n.$$

We have two linearly independent series solutions,

$$a_0 = 1, \quad a_1 = 0 \quad \rightarrow \quad a_{2n} = (-1)^n \frac{k^{2n}}{(2n)!} \quad \rightarrow \quad y_0(x) = \sum_{n=0}^{\infty} (-1)^n \frac{(kx)^{2n}}{(2n)!}$$

$$a_0 = 0, \quad a_1 = 1 \quad \rightarrow \quad a_{2n+1} = (-1)^n \frac{k^{2n+1}}{(2n+1)!} \quad \rightarrow \quad y_1(x) = \sum_{n=0}^{\infty} (-1)^n \frac{(kx)^{2n} x}{(2n+1)!}$$

Series Solution of the Differential Equation

Recalling the Taylor expansions of sine and cosine, we can deduce

$$y_0(x) = \sum_{n=0}^{\infty} (-1)^n \frac{(kx)^{2n}}{(2n)!} = \cos(kx),$$

$$y_1(x) = \sum_{n=0}^{\infty} (-1)^n \frac{(kx)^{2n} x}{(2n+1)!} = \frac{1}{k} \sin(kx),$$

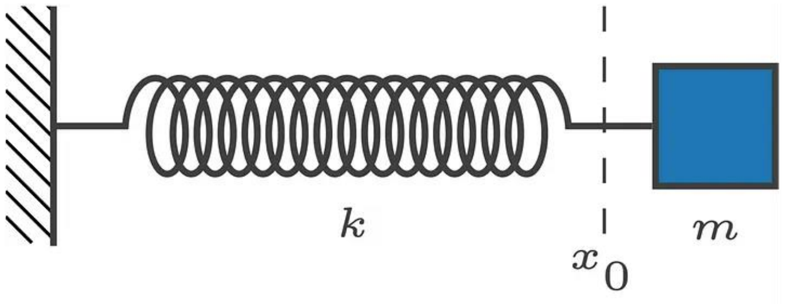
$$y(x) = A y_0(x) + B y_1(x) = A \cos(kx) + B' \sin(kx).$$

This method is called the series solution of the DE.

This technique becomes more useful in more complicated differential equations, as we will see.

Classical Harmonic Oscillator

A particle of mass m is attached to a spring whose length at rest is x_0.



If the particle is moved along the x-axis, the spring will exert a restoring force that acts in the opposite direction of the displacement,

$$F = -k(x - x_0).$$

Suppose the particle is initially at the position $x(0)$ and velocity $v(0)$, and we want to predict the state of the particle at time t.

Classical Harmonic Oscillator

By Newton's second law, we have

$$F(x) = -k[x(t) - x_0] = m\frac{d^2x(t)}{dt^2}.$$

If we make the substitution $x(t) - x_0 = X(t)$, the DE is converted to

$$-kX(t) = m\frac{d^2X(t)}{dt^2}.$$

which can be easily solved to yield

$$x(t) = x_0 + A\cos(\omega t) + B\sin(\omega t), \quad \omega = \sqrt{k/m} = 2\pi f.$$

The undetermined coefficients A and B are specified by the initial conditions,

$$A = x(0) - x_0, \qquad B = \frac{v(0)}{\omega}.$$

Classical Harmonic Oscillator

We can define the potential energy w.r.t. the equilibrium position

$$V(x) = -\int_c \vec{F} \cdot d\vec{s} = -\int_{x_0}^{x} F(x)\, dx = \frac{1}{2}k(x - x_0)^2 = \frac{m\omega^2}{2}(x - x_0)^2.$$

As usual, the Hamiltonian function of the system

$$H(x) = T + V(x) = \frac{p^2}{2m} + \frac{m\omega^2}{2}(x - x_0)^2$$

represents the total energy of the system.

The potential and kinetic energy change with time, but their sum remains constant due to energy conservation.

Quantum Harmonic Oscillator

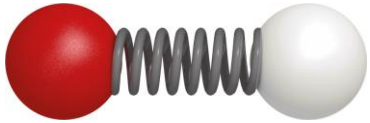
From now on, we will redefine the natural length (equilibrium position) of the spring as $x = 0$, which converts the Hamiltonian to

$$H(x) = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2.$$

The quantum mechanical operator corresponding to this Hamiltonian is

$$\hat{H}(x) = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2.$$

This quantum harmonic oscillator Hamiltonian is widely used as the simplest model for describing molecular vibrations.



Series Solution

The Schrödinger equation is

$$\hat{H}(x)\psi(x) = E\psi(x),$$

which is expressed as

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{m\omega^2}{2}x^2\psi(x) = E\psi(x).$$

Inserting the series solution $\psi(x) = \sum_n a_n x^n$

leads to the relations $-\frac{\hbar^2}{m}a_2 - Ea_0 = 0, \quad -\frac{3\hbar^2}{m}a_3 - Ea_1 = 0,$

$$-\frac{\hbar^2}{2m}(n+1)(n+2)a_{n+2} - Ea_n + \frac{m\omega^2}{2}a_{n-1} = 0.$$

Series Solution

Such a three-term relations are not easy to handle, and the answer also would not be so intuitive.

Instead of the direct approach, we insert an ansatz

$$\psi(x) = f(x)e^{-\alpha x^2/2}, \quad \alpha = \frac{m\omega}{\hbar},$$

into the original DE and get a new DE in terms of $f(x)$,

$$f''(x) - 2\alpha x f'(x) + (K - \alpha)f(x) = 0, \quad K = \frac{2mE}{\hbar^2}.$$

Apply the series solution approach gives a two-term recurrence relation

$$f(x) = \sum_{n=0}^{\infty} c_n x^n, \quad \rightarrow \quad c_{n+2} = \frac{\alpha + 2n\alpha - K}{(n+1)(n+2)} c_n$$

Series Solution

To satisfy the boundary condition for the wavefunction $\lim_{x\to\pm\infty} \psi(x) = 0$, the series must terminate after finite terms, which means

$$\frac{\alpha + 2v\alpha - K}{(v+1)(v+2)} = 0$$

for a certain v. This forces K to have the value of

$$K = (2v+1)\alpha, \quad v = 0, 1, 2 \cdots .$$

which makes the series terminate at the order v.

Combining this result with $K = 2mE/\hbar^2$ and $\alpha = m\omega/\hbar$ gives us the quantized energies

$$E = \left(v + \frac{1}{2}\right)\hbar\omega.$$

Series Solution

Once v is determined, the recursion relation becomes

$$c_{n+2} = \frac{2\alpha(n-v)}{(n+1)(n+2)} c_n.$$

Therefore, the solutions are

$$\psi_v(x) = \begin{cases} (c_0 + c_2x^2 + \cdots c_v x^v)e^{-\alpha x^2/2}, & v \text{ even} \\ (c_1 x + c_3 x^3 + \cdots c_v x^v)e^{-\alpha x^2/2}, & v \text{ odd} \end{cases}.$$

These solutions can be compactly written as

$$\psi_v(x) = A_v H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2},$$

where A_v is the normalization constant and $H_v(x)$ is the Hermite polynomial of order v.

Basic Properties of the Solutions

$$H_n(x) = e^{x^2}\left(-\frac{d}{dx}\right)^n e^{-x^2}, \quad H_{n+1}(x) = 2xH_n(x) - H_n'(x)$$

$$\psi_v(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4} H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2}$$

$$\begin{aligned}
H_0(x) &= 1,\\
H_1(x) &= 2x,\\
H_2(x) &= 4x^2 - 2,\\
H_3(x) &= 8x^3 - 12x,\\
H_4(x) &= 16x^4 - 48x^2 + 12,\\
H_5(x) &= 32x^5 - 160x^3 + 120x,\\
H_6(x) &= 64x^6 - 480x^4 + 720x^2 - 120,\\
H_7(x) &= 128x^7 - 1344x^5 + 3360x^3 - 1680x,\\
H_8(x) &= 256x^8 - 3584x^6 + 13440x^4 - 13440x^2 + 1680,\\
H_9(x) &= 512x^9 - 9216x^7 + 48384x^5 - 80640x^3 + 30240x,\\
H_{10}(x) &= 1024x^{10} - 23040x^8 + 161280x^6 - 403200x^4 + 302400x^2 - 30240.
\end{aligned}$$

The first three solutions:

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2},$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2},$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}.$$

https://en.wikipedia.org/wiki/Hermite_polynomials

Basic Properties of the Solutions

The energies of the solution wavefunctions follow

$$E = \left(v + \frac{1}{2}\right)\hbar\omega, \quad v = 0, 1, 2 \cdots$$

which forms a ladder with an equal spacing of $\hbar\omega$.

The smallest quantum number for harmonic oscillator is $v = 0$.

Note that this is different from the particle-in-a-box problem, where the quantum number started from 1.

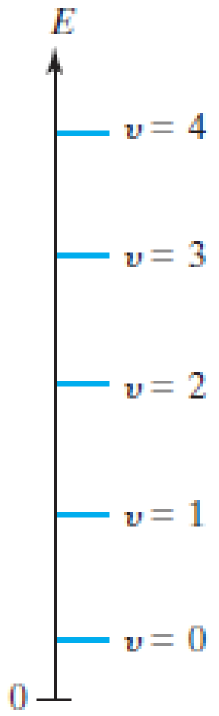
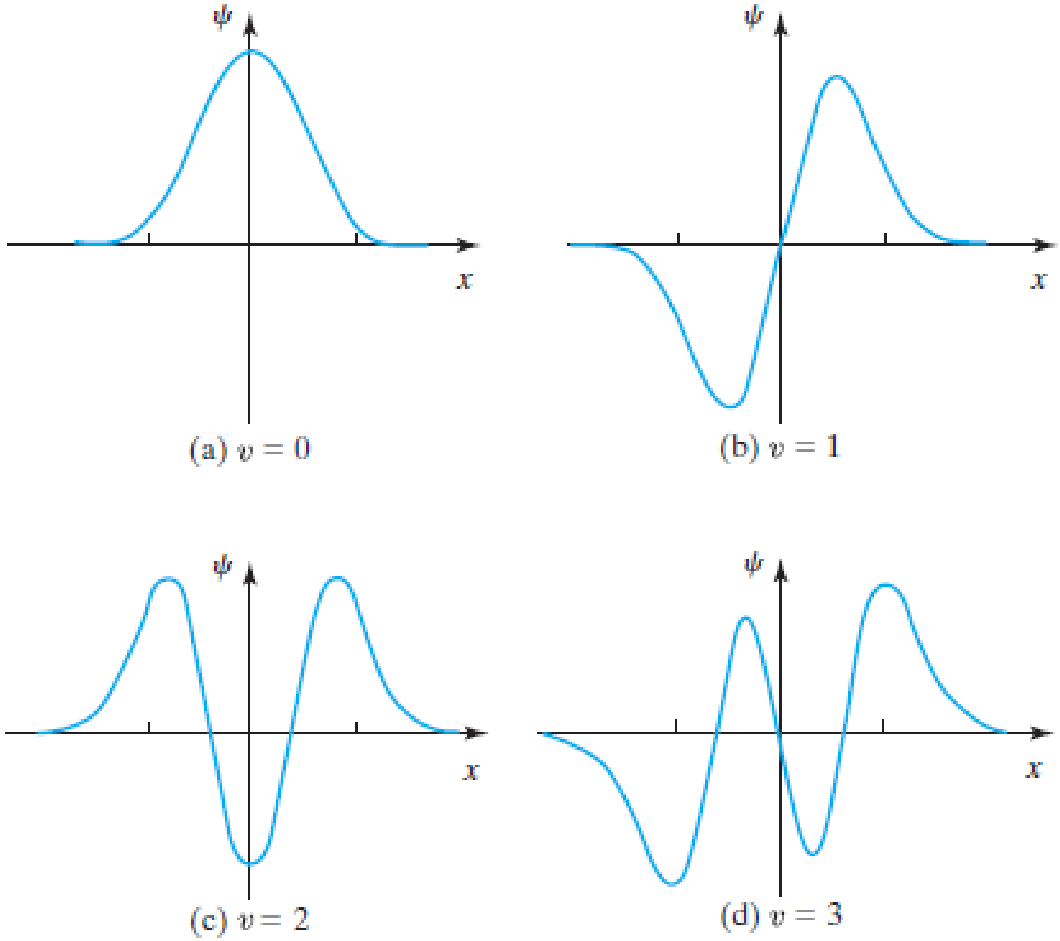


FIGURE 4.1 Lowest five energy levels for the one-dimensional harmonic oscillator.

Levine, I. N. *Quantum Chemistry*, 7th ed.

Basic Properties of the Solutions



The solution wave function with the quantum number v has v nodes.

$$\psi_v(x) \sim H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2}$$

The wavefunctions also exhibit tunneling through classically forbidden region.

Example: $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}.$

Levine, I. N. *Quantum Chemistry*, 7th ed.

Ladder Operator Formalism

The classical Hamiltonian can be factorized into

$$H(x) = \frac{m\omega^2 x^2}{2} + \frac{p^2}{2m} = \omega\left(\sqrt{\frac{m\omega}{2}}x - i\frac{p}{\sqrt{2m\omega}}\right)\left(\sqrt{\frac{m\omega}{2}}x + i\frac{p}{\sqrt{2m\omega}}\right)$$

However, for the quantum Hamiltonian, we have an additional term due to the commutation relation $[\hat{x}, \hat{p}] = i\hbar$:

$$\hat{H}(x) = \frac{m\omega^2 \hat{x}^2}{2} + \frac{\hat{p}^2}{2m} = \omega\left(\sqrt{\frac{m\omega}{2}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\omega}}\right)\left(\sqrt{\frac{m\omega}{2}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\omega}}\right) + \frac{\hbar\omega}{2}$$

$$= \hbar\omega\left[\sqrt{\frac{\alpha}{2}}\left(\hat{x} - \frac{i}{\hbar\alpha}\hat{p}\right)\right]\left[\sqrt{\frac{\alpha}{2}}\left(\hat{x} + \frac{i}{\hbar\alpha}\hat{p}\right)\right] + \frac{\hbar\omega}{2}$$

$$= \hbar\omega\left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right)$$

Ladder Operator Formalism

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right), \quad [\hat{a}, \hat{a}^\dagger] = 1$$

Then we have

$$[\hat{H}, \hat{a}] = -\hbar\omega\hat{a}, \quad [\hat{H}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger.$$

Meanwhile, the Schrödinger equation is

$$\hat{H}\psi_v(x) = E_v\psi_v(x),$$

which can be combined with the commutation relations and yield

$$\hat{H}\hat{a}\psi_v(x) = (E_v - \hbar\omega)\hat{a}\psi_v(x), \quad \hat{H}\hat{a}^\dagger\psi_v(x) = (E_v + \hbar\omega)\hat{a}^\dagger\psi_v(x).$$

Ladder Operator Formalism

$$\hat{H}\hat{a}\psi_v(x) = (E_v - \hbar\omega)\hat{a}\psi_v(x), \quad \hat{H}\hat{a}^\dagger\psi_v(x) = (E_v + \hbar\omega)\hat{a}^\dagger\psi_v(x).$$

This means that $\hat{a}\psi_v(x)$ and $\hat{a}^\dagger\psi_v(x)$ are also the solutions of the Schrödinger equation, with the energies $E_v - \hbar\omega$ and $E_v + \hbar\omega$.

Therefore, the set of solutions

$$\hat{a}^n\psi_v(x) \quad \text{and} \quad (\hat{a}^\dagger)^n\psi_v(x),$$

constitutes an “energy ladder” with a uniform spacings of $\hbar\omega$.

The ladder must terminate at some point, as the energy cannot be negative. So there exists the lowest energy solution which satisfies

$$\hat{a}\psi_0(x) = 0.$$

Ladder Operator Formalism

$$\hat{a}\psi_0(x) = 0 \quad \rightarrow \quad \psi_0'(x) + \alpha x \psi_0(x) = 0.$$

This is first-order differential equation, which can be easily solved by separation of variables:

$$\psi_0(x) = Ae^{-\alpha x^2}.$$

The undetermined constant A can be specified by normalization condition

$$\int_{-\infty}^{\infty} |\psi_0(x)|^2 \, dx = 1,$$

which gives

$$A = \left(\frac{\alpha}{\pi}\right)^{1/4}.$$

Ladder Operator Formalism

What are the higher-energy wavefunctions? We have seen that

$$(\hat{a}^\dagger)^n \psi_0(x) \sim \psi_n(x),$$

but we did not determine the normalization constant.
From the relations

$$\int_{-\infty}^{\infty} \psi_n^*(x) \hat{a}^\dagger \hat{a} \psi_n(x)\, dx = n, \quad \int_{-\infty}^{\infty} \psi_n^*(x) \hat{a} \hat{a}^\dagger \psi_n(x)\, dx = n + 1,$$

we can infer

$$\hat{a}\psi_n(x) = \sqrt{n}\psi_{n-1}(x), \quad \hat{a}^\dagger \psi_n(x) = \sqrt{n+1}\psi_{n+1}(x).$$

Validation of Eigenfunction Expression

$$H_n(z) = e^{z^2}\left(-\frac{d}{dz}\right)^n e^{-z^2}$$

$$\hat{a}^\dagger = \sqrt{\frac{1}{2}}\left(\sqrt{\alpha}x - \frac{1}{\sqrt{\alpha}}\frac{d}{dx}\right)$$

We now use the mathematical induction. If

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4} H_n(\sqrt{\alpha}x)e^{-\alpha x^2/2}$$

is satisfied, we have

$$\psi_{n+1}(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left[\frac{1}{\sqrt{2(n+1)}}\left(\sqrt{\alpha}x - \frac{1}{\sqrt{\alpha}}\frac{d}{dx}\right)\right]\left[e^{\alpha x^2/2}\left(-\frac{1}{\sqrt{\alpha}}\frac{d}{dx}\right)^n e^{-\alpha x^2}\right]$$

$$= \frac{1}{\sqrt{2^{n+1}(n+1)!}}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{\alpha x^2/2}\left(-\frac{1}{\sqrt{\alpha}}\frac{d}{dx}\right)^{n+1} e^{-\alpha x^2}$$

$$= \frac{1}{\sqrt{2^{n+1}(n+1)!}}\left(\frac{\alpha}{\pi}\right)^{1/4} H_{n+1}(\sqrt{\alpha}x)e^{-\alpha x^2/2}.$$

Matrix Form of the Ladder Operators

In the Harmonic oscillator eigenbasis $|n\rangle$, the matrix form of the ladder operators are

$$\hat{a}^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & 0 & \cdots \\ 0 & 0 & 0 & 2 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad \hat{a} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \cdots \\ 0 & 0 & 0 & 0 & 2 & \cdots \\ 0 & 0 & 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

To connect these matrices to $\hat{x}$ and $\hat{p}$, we use the relations

$$\hat{x} = \frac{1}{\sqrt{2\alpha}}(\hat{a}^\dagger + \hat{a}), \quad \hat{p} = -i\hbar\sqrt{\frac{\alpha}{2}}(\hat{a}^\dagger - \hat{a}).$$

Matrix Form of the Ladder Operators

The products of the ladder operators are given as

$$\hat{a}\hat{a}^\dagger = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 2 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 3 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 4 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 5 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad \hat{a}^\dagger\hat{a} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 2 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 3 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 4 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

where we can recognize again the commutation relation $[\hat{a}, \hat{a}^\dagger] = 1$.

Also, $\hat{a}^\dagger\hat{a}$ is called number operator due to the property

$$\hat{a}^\dagger\hat{a}\,|n\rangle = n\,|n\rangle\,.$$

Statistical Thermodynamics of QHO

$$\hat{x} = \frac{1}{\sqrt{2\alpha}}(\hat{a}^\dagger + \hat{a}), \quad \hat{p} = -i\hbar\sqrt{\frac{\alpha}{2}}(\hat{a}^\dagger - \hat{a})$$

For the wavefunction $\psi_n(x)$, we have

$$\langle x \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{x}\psi_n(x)\,dx = 0, \quad \langle p \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{p}\psi_n(x)\,dx = 0.$$

This reflects the fact that the Hamiltonian is symmetric. However,

$$\langle x^2 \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{x}^2\psi_n(x)\,dx = \frac{2n+1}{2}\frac{\hbar}{m\omega},$$

$$\langle p^2 \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{p}^2\psi_n(x)\,dx = \frac{2n+1}{2}\hbar m\omega.$$

Statistical Thermodynamics of QHO

At zero temperature, only the ground state ($n = 0$) is populated.

$$\sigma_x = \sqrt{\langle x^2 \rangle_0 - (\langle x \rangle_0)^2} = \sqrt{\frac{\hbar}{2m\omega}},$$

$$\sigma_p = \sqrt{\langle p^2 \rangle_0 - (\langle p \rangle_0)^2} = \sqrt{\frac{\hbar m\omega}{2}}.$$

This satisfies the lower bound for the uncertainty principle,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

Statistical Thermodynamics of QHO

At nonzero temperature, all states are populated according to Boltzmann distribution. What is the energy expectation value?

To answer this question, we need to evaluate the expectation value

$$E(T) = \sum_{n=0}^{\infty} \langle \hat{H} \rangle_n P_n(T),$$

where the population $P_n(T)$ is

$$P_n(T) = \frac{\exp[-\beta\hbar\omega(n+1/2)]}{\sum_{n=0}^{\infty} \exp[-\beta\hbar\omega(n+1/2)]}, \quad \beta = \frac{1}{kT}.$$

Statistical Thermodynamics of QHO

Meanwhile,

$$\langle \hat{H} \rangle_n = \frac{\langle p^2 \rangle}{2m} + \frac{m\omega^2}{2}\langle x^2 \rangle = \left(n + \frac{1}{2}\right)\hbar\omega.$$

Therefore

$$\langle \hat{H} \rangle(T) = \frac{\sum_{n=0}^{\infty} \hbar\omega(n+1/2)\exp[-\beta\hbar\omega(n+1/2)]}{\sum_{n=0}^{\infty}\exp[-\beta\hbar\omega(n+1/2)]}$$

Let us evaluate the summations:

$$\sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right] = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}},$$

$$\sum_{n=0}^{\infty} \hbar\omega\left(n+\frac{1}{2}\right)\exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right] = \frac{\hbar\omega}{2}\frac{e^{\beta\hbar\omega/2} + e^{-\beta\hbar\omega/2}}{(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2})^2},$$

Statistical Thermodynamics of QHO

The final result is

$$\langle\hat{H}\rangle(T) = \frac{\hbar\omega}{2}\frac{e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$$

At high temperature,

$$\lim_{T\to\infty}\langle\hat{H}\rangle(T) = \frac{kT}{2},$$

which recovers the classical result (correspondence principle). On the other hand, the opposite limit is

$$\lim_{T\to 0}\langle\hat{H}\rangle(T) = \frac{\hbar\omega}{2}.$$